CARBON-AIR ELECTRODES
FOR LOW TEMPERATURE FUEL CELLS

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I. INTRODUCTION

The economy of a terrestrial, low temperature fuel cell system depends strongly on the feasibility of using air at atmospheric pressure. High current densities are required to keep battery weight and size down; simple operation, preferably at atmospheric pressure, is desired to avoid costly and energy-consuming accessories. Last, but not least, the use of noble metal catalysts and expensive structural materials must be restricted to a minimum.

At the present time, low temperature, acidic-electrolyte, fuel cell systems have not reached the development stage which would indicate their practical utilization in the near future. For this reason, the discussion will be limited to alkaline electrolytes only. With hydrophobic carbon electrodes, it is a matter of technical choice whether liquid or immobilized electrolytes are used; therefore, no differentiation will be made.

II. DISCUSSION

1. The Performance of Carbon-Air Electrodes.

a) Comparison of Polarization Curves. - The potential of an electrode at a given load is dependent on the activity of the catalytic system used. Carbon-oxygen (air) electrodes function as hydrogen, peroxide-producing, gas-diffusion electrodes, and for this reason show a strong dependence on the peroxide-decomposing capability of the electrode surface. (1)

Figure 1 shows the polarization curves of three differently catalyzed carbon electrodes. Characteristic is the high voltage level of the Pt-catalyzed cathodes—Pt is deposited in a quantity of 1 milligram per cm² of geometric surface. A very remarkable performance is shown

by the third electrode, containing no specially added metals—only the peroxide-decomposing catalytic activity of the basic $CoOAl_2O_3$ spinel-containing carbon is demonstrated. (2) While the initial performance level is lower, the current-carrying ability is greater at very high current densities.
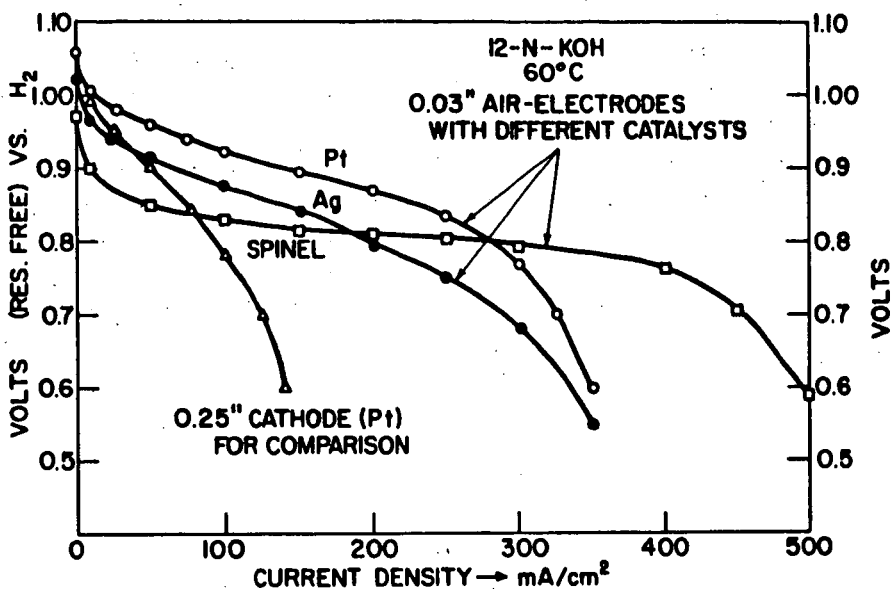
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Fig. 1   Electrode Polarization Curves Employing Different Catalysts (Linear Diagram).

The upper-three curves of Fig. 1 were obtained with so-called "fixed-zone", 0.03-inch thick composite electrodes consisting of a repellent porous nickel plaque (0.008-inch thick) coated with layers of catalyzed carbon. (3) The fourth curve in Fig. 1 was obtained with a platinum-catalyzed, 0.25-inch thick carbon electrode (1 mg Pt/cm^2). While pure oxygen performance (not shown) of 0.25-inch and 0.03-inch electrodes is essentially equal, the performance with air is very different. The thicker electrode is clearly diffusion-limited.

The same voltage-current curves of Fig. 1 (linear diagram) are replotted in Fig. 2 using a logarithmic abscissa. The similarity in elec-

trochemical behavior of the four electrodes becomes more apparent in
the second figure. The Tafel slopes are identical (40 to 50 mv per
decade at low current densities), but the voltage levels are different
in accordance with the chosen catalyst. Also different is the extent
of the "mass-transport limitation" (as expected, considering the dif-
ference in electrode thicknesses). The cross-over of the "spinel-
catalyzed" thin electrode is not accidental—this characteristic is
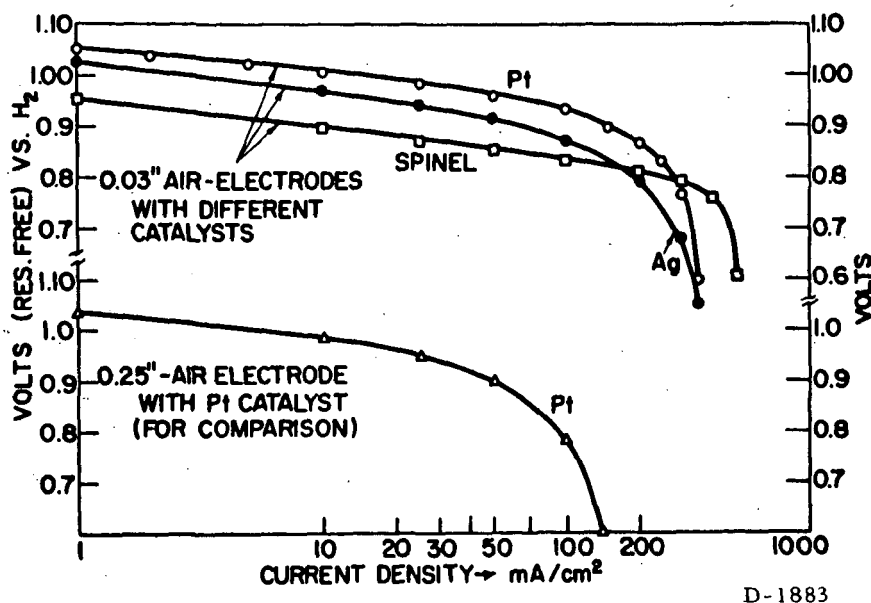consistently observed.

Fig. 2   Electrode Polarization Curves Employing Different
Catalysts (Logarithmic Diagram).

b) Operational Life of Air Electrodes. - Life of the electrodes
depends, first of all, upon the current density. Current density deter-
mines the operational voltage (as Figs. 1 and 2 demonstrate). The
"polarization level" (terminal voltage minus the voltage drop in the
resistive components of the cell) is a more decisive parameter than
the "terminal voltage". This "resistance-free" voltage can be deter-
mined by means of current interrupter devices (4), or suitably placed
reference electrodes.

The relationship between current density and operational life seems to be an exponential function. Doubling the current density usually decreases life to one-fourth the time, or vice versa; cutting the current density in half prolongs the electrode life fourfold. This should be considered only as a "rule-of-thumb" fitting our present experience.

Figure 3 shows the performance life of 1965 Union Carbide thin electrodes operating on a continuous load corresponding to 100 A/SF (105 ma/cm²). It should be noted that CO_2-free (scrubbed) air has been used.
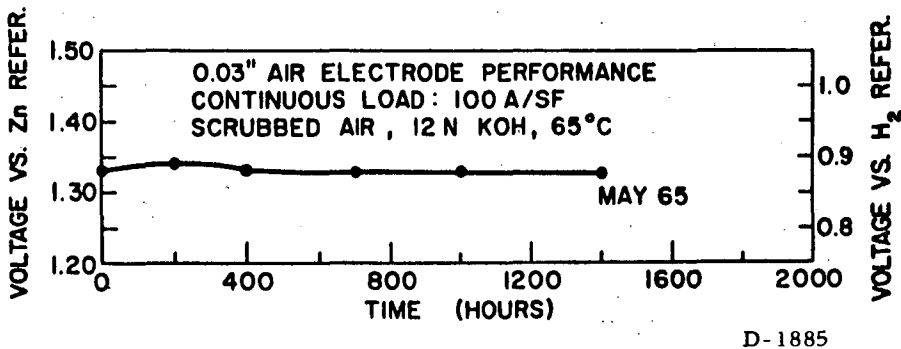
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Fig. 3 Operational Life of Union Carbide Fixed-Zone, Air Electrodes(1965).

2. The Effect of Carbon Dioxide from the Air.

The approximate 0.03% CO_2 contained in air is known to be detrimental to alkaline cell performance. Consequently, most tests are performed with CO_2-free air; and less data are available about the nature and extent of carbon dioxide's damaging effects.

However, for economical operation of larger fuel cell batteries, the cost of air scrubbing is important. In addition, size and weight problems are introduced by air-scrubbing accessories. Therefore, an attempt has been made to answer a few principal questions concerning this matter:

  a) The effect of carbonate in the electrolyte;

  b) The rate of CO_2-pickup through the operating electrode;

c) The effect of CO_2 on electrode life (catalysts, variation in electrolytes, etc.), and

d) Possible explanation of the effects.

a) The Effect of Carbonate in the Electrolyte. - For comparison, two identical cells were operated in 6 molar KOH containing 0.4 mol potassium carbonate, and 6 molar KOH containing 1.0 mol potassium carbonate. The air supplied to the cell was cleaned in a gas wash tower containing KOH; no additional CO_2 was absorbed during operation. No noticeable difference in performance was observed.

b) Rate of CO_2-Contamination through the Operating Electrode. - The speed of CO_2-pickup from the air through the wall of cathodes was first tested with 0.25-inch carbon cathodes continuously exposed to room air in a concentric, triangular, 7-cell battery (5). Table I gives the data which show that the CO_2-takeup from the air (for 6 M KOH) was rapid during the first few days, then slowed down considerably.

TABLE I

RATE OF CO_2-CONTAMINATION OF 6 M KOH
IN AIR-EXPOSED CELLS (15 ma/cm^2 LOAD)

Time Elapsed Since Exposure of Cathodes (6 M KOH) to Air	Titrated M CO_3^{--}
72 Hours = 3 Days	0.4 M
720 Hours = 4 Weeks	1.0 M
2160 Hours □ 3 Months	2.5 M

Adding KOH pellets to the partially neutralized caustic solution until the OH^- ion concentration corresponded to 6 M KOH restored the original performance.

c) The Effect of CO_2 on Electrode Life. - The 0.25-inch carbon electrodes used in the concentric (triangular) cells, mentioned above, carried no special metal catalyst. Most of the test cells survived 4000 hours at a current density of 15 ma/cm^2; some operated for 7000 hours. Cell life was only about 800 hours under the same conditions of operation and air exposure when 0.25-inch, platinum-catalyzed (1 mg/cm^2) cathodes were employed.

Figure 4 illustrates the average results of these tests. The voltage level of the noble metal-catalyzed cathodes was higher, but life was far shorter.
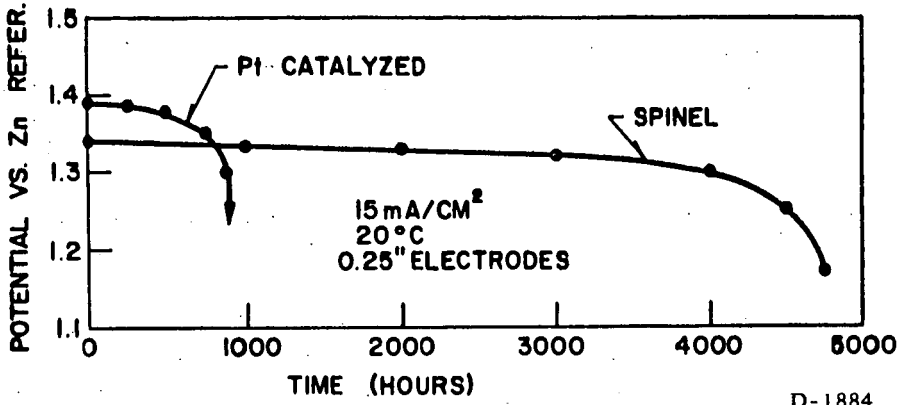

Fig. 4   Performance with CO_2-Containing Air, Comparing Noble Metal-Catalyzed vs. Spinel-Catalyzed Cathodes.

In another series, platinum-catalyzed, thin electrodes (1963) were operated with CO_2-containing air, using 6 N KOH for one set of cells, and 6 N NaOH for the other. Figure 5 shows the results—the cathodes in NaOH outlived the cathodes in KOH by a wide margin, again at the cost of the voltage level, however.
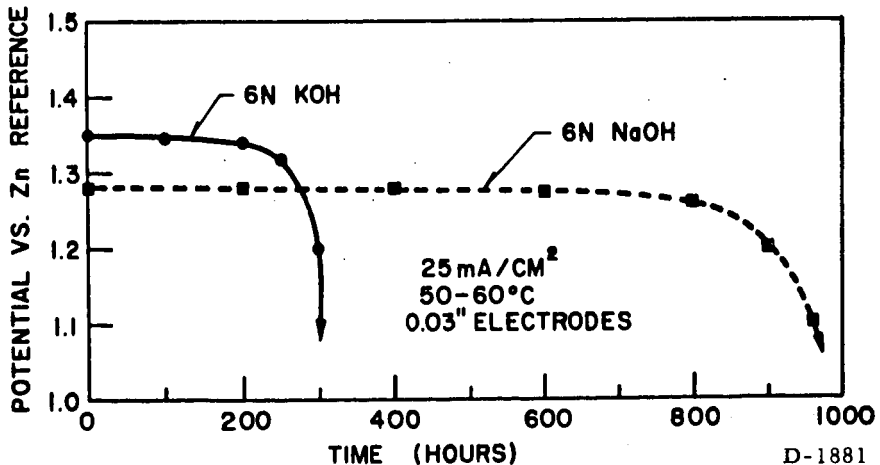

Fig. 5   Performance with CO_2-Containing Air, Comparing Platinum-Catalyzed Cathodes—6 N KOH vs. 6 N NaOH.

A third combination (uncatalyzed electrodes in NaOH electrolyte) did not look promising from the cell-performance standpoint at that time. This combination will be tried in the future using newer, more active electrodes.

d) <u>Possible Explanation of Effects</u> - Physical examination of the CO_2-damaged electrodes always revealed a mechanical blockage. It seems that the degree of repellency of an electrode determines the degree of resistance against CO_2 damage. NaOH is less wetting than KOH, and platinum-catalyzed electrodes are less repellent than electrodes without platinum catalyzation. CO_2-damage is also current-density dependent; a heavily polarized air electrode has a shorter life in the same electrolyte than does one showing a lesser degree of polarization.

Experiments with porous metal electrodes indicate that "wet"-operated electrodes (gas pressure balance) have an extremely low tolerance for CO_2. The pores of such electrodes plug within a few hours, and physical damage (possibly by expanding carbonate) is irreversible. Carbonate-plugged, 0.25-inch carbon electrodes were usually permanently damaged, and could not be revived. However, the newer thin composite electrodes have frequently been washed and reused.

III. CONCLUSIONS

Carbon-containing cathodes seem to be the most desirable electrodes for high-power density, economical, air-fuel cells. The fuel source for such low temperature cells may be hydrogen from hydrocarbon reformer units, or hydrogen from alcohol or ammonia converters.

At present, CO_2 removal is necessary during air operation in order to attain long life at high current densities. However, recognition of the nature of carbon dioxide effects on today's electrodes is the first step towards possible future remedy.

In the author's opinion, of all the available cathodes, the carbon electrode is the least sensitive to carbon dioxide damage.

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